Relative laboratory volatility of Dicamba in closed dome systems with varied pH, temperature, and relative humidity

Report:	MRID 51049001. Wanner, U. 2020. Volatilization Assessment for Dicamba via Quantitative Humidome Set-Up. Unpublished study performed by Symbiotic Research LLC-Subsidiary of Tentamus GmbH, Mount Olive, New Jersey, and Genesis Midwest Laboratories, Neillsville, Wisconsin, and sponsored and submitted by BASF, Research Triangle Park, North Carolina. Symbiotic Research Report No.: SR20191207A and Study No.: NG018. BASF Registration Document No. (DocID): 2020/2001268. Experiment initiated on July 24, 2019 and terminated November 12, 2019 (p. 13). Final report issued February 3, 2020.
Document No.:	MRID 51049001
Guideline:	Non-guideline
Statements:	The study was not conducted in compliance with U.S. EPA FIFRA (40 CFR Part 160) Good Laboratory Practice (GLP) standards, which are compatible with OECD GLP standards; however, "all efforts were made to ensure that the data is clearly captured and documented, and that the final report reflects all obtained results completely and correctly" (p. 3). Signed and dated GLP Compliance, Data Confidentiality, and Certification of Authenticity statement statements were provided (pp. 2-3, 5). An unsigned Quality Assurance statement was provided (there were no 'in-life/laboratory' audits and the raw data was not reviewed by an independent QAU; p. 4).
Classification:	This study is **supplemental, non-guideline**. The compositions of the test substances were not reported, and test substance storage was not reported. The test soil was only partially characterized. The test soil consisted of 50% Redi-Earth, a soil with a large amount of sphagnum peat moss, which would make it very high in organic carbon. Results of this study should not be used quantitatively except for soils with an organic carbon content greater than or equal to that of peat soil. Differences in volatility should be regarded as relative, not absolute. The method LOD was not reported.

PC Code:	100094 (Dicamba BAPMA)	
Final EPA Reviewer:	**Chuck Peck** Senior Fate Scientist	**Signature:** Chuck Peck **Date:** 2020.10.22 10:17:47 -04'00'
CDM/CSS-Dynamac JV Reviewers:	Lisa Muto, M.S., Environmental Scientist	Signature: Lisa Muto Date: 04/24/2020
	Joan Gaidos, Ph.D., Environmental Scientist	Signature: Date: 04/24/2020

This Data Evaluation Record may have been altered by the Environmental Fate and Effects Division subsequent to signing by CDM/CSS-Dynamac Joint Venture personnel. The CDM/CSS-Dynamac JV role does not include establishing Agency policies

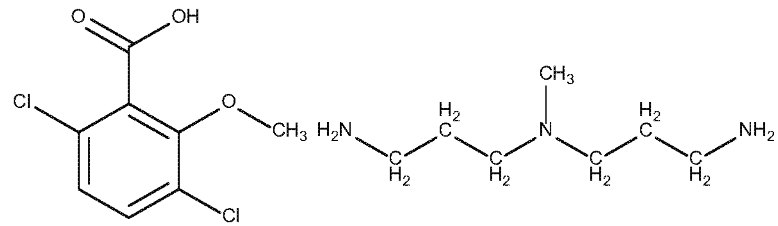
Executive Summary

In a laboratory study, the relative dicamba volatility of Engenia® was investigated on partially characterized soil (50% sandy loam soil and 50% Redi-Earth & Seedling Potting Mix) under aerobic soil conditions for a period of *ca*. 24 hours with varied solution pHs under ambient environmental conditions, varied temperatures with ambient relative humidity (*ca*. 35-50%), and varied relative humidity at *ca*. 30°C and *ca*. 40°C. Engenia® tank mixtures with partners were prepared using Cornerstone Plus®, Roundup PowerMax®, Raptor®, Reflex®, and Outlook® and the relative dicamba volatility of the tank mixtures were investigated with the test soil for a period of *ca*. 24 hours with varied solution pHs under ambient environmental conditions.

Soil samples were treated at a target application rate of *ca*. 0.56 kg a.e./ha (0.5 lb a.e. dicamba/A). Four replicates for each test condition were examined in the study. Mixed Cellulose Ester (MCE) filter samples were collected for 24 hours after application at a target flow rate of 2.00 ± 0.10 L/minute. The MCE samples were extracted using methanol then centrifuged or filtered to eliminate precipitate, and dicamba was quantitated using LC-MS/MS. Method validation data was incomplete. No analyses of dicamba in soil were performed. Mass of dicamba, 24-hour average dicamba concentrations, 24-hour average flux rates, and the percent of applied dicamba collected on the sorbent material was generated for each replicate.

The volatilization of dicamba increased with lowered pH in Engenia® alone trials and Engenia® tank mix spray solutions trials. Maximum volatilized dicamba was observed at pH 2 for Engenia® and all Engenia® tank mixes, except Engenia® + Reflex®. The pH range of 6.0-7.0 generally corresponded to reduced volatilization. Increased variability of the replicate data occurred with lowered pH/increased dicamba volatility.

A trend of increased volatilization also corresponded with higher temperatures (>40°C) and higher relative humidity with higher temperatures.



Dicamba BAPMA [Dicamba -N,N-Bis(3-aminopropyl)methylamine]

I. Material and Methods

A. Materials

1. Test Materials

Table 1a. Properties of Test Materials

Property	Engenia®	Cornerstone Plus®	Roundup PowerMAX®	Reflex®	Raptor®	Outlook®
Product Name	Engenia®	Cornerstone Plus®	Roundup PowerMAX®	Reflex®	Raptor®	Outlook®
BAS No./Code	BAS 183 22 H [dicamba in the form of its N,N-Bis-(3-amino propyl)methyl amine (BAPMA) salt]	BAS 683 SU H	BAS 683 SP H	BAS 9091 1H	BAS 720 01H	BAS 656 11H
Formulation Type	SL formulation (former code No. 183 WB H), nominal content dicamba (a.e.) 600 g/L	Not reported				
Typical end-use product?	Yes	Not reported				
Function	Herbicide	Herbicide	Herbicide	Herbicide	Herbicide	Herbicide
Contaminants and/or impurities	Dicamba (a.e.): 48.95 % or 604.4 g/L Contaminants not reported	356 g/L Glyphosate (as isopropylamine salt) Contaminants not reported	540 g/L Glyphosate (as potassium salt) Contaminants not reported	240 g/L fomesafen (as sodium salt)	120 g/L imazamox (as ammonium salt) Contaminants not reported	720 g/L dimethenamid-P Contaminants not reported
Manufacture #	Not reported					
Batch ID	7195N01DD	A5080671127	MNZT1020AJ	MHA7B19-HB1	6018M01MV	8089B01BQ

Property	Engenia®	Cornerstone Plus®	Roundup PowerMAX®	Reflex®	Raptor®	Outlook®
Type of radiolabel	Not radiolabeled					
CAS #	1918-00-9 (dicamba) 105-83-9 (BAPMA)	1071-83-6 (glyphosate)	1071-83-6 (glyphosate)	72178-02-0 (fomesafen)	114311-32-9 (imazamox)	163515-14-8 (dimethenamid-P)
Chemical structure	See image above	Not applicable				
Storage stability	Not reported Keep at room temperature (5-35°C).	Not reported				
pH	6.5	Not reported				

Data obtained from pp. 14-15, Table 1, p. 15, and Appendix 1, p. 50, of the study report.

Table 1b. Properties of Tank Mixtures

Property	Tank Mix 1	Tank Mix 2	Tank Mix 3	Tank Mix 4	Tank Mix 5	Tank Mix 6
Tank Mix Component 1	Engenia® (12.8 fl. oz./A) (0.012 mL/tray)	Engenia® (12.8 fl. oz./A) (0.012 mL/tray)	Engenia® (12.8 fl. oz./A) (0.012 mL/tray)	Engenia® (12.8 fl. oz./A) (0.012 mL/tray)	Engenia® (12.8 fl. oz./A) (0.012 mL/tray)	Engenia® (12.8 fl. oz./A) (0.012 mL/tray)
Tank Mix Component 2	None	Cornerstone Plus® (32 fl. oz./A) (0.030 mL/tray)	Roundup PowerMAX® (32 fl. oz./A) (0.030 mL/tray)	Reflex® (16 fl. oz./A) (0.015 mL/tray)	Raptor® (4 fl. oz./A) (0.004 mL/tray)	Outlook® (21 fl. oz./A) (0.020 mL/tray)
Final pH (non-adjusted)	6.5	4.9	4.7	6.6	6.5	6.5

Data obtained from pp. 17-18, Table 2, p. 18, and Table 11, p. 34, of the study report

2. Storage Conditions

Test substance storage was not reported (pp. 14-15, 17-18).

3. Soil

Soil properties are provided in **Table 2**. According to ASTM STP1587, on which the humidome studies are based, in order to minimize variability due to the soil composition, a one to one mixture of field soil and Redi-Earth was used. Although different soil types may impact volatility, the use of this standard soil mixture was selected to help reduce the impact of the variability of soil content. According to information obtained from the Internet (http://www.sungro.com/professional-product/sunshine-redi-earth-plug-seedling/), Redi-Earth is a mixture of fine sphagnum peat moss, dolomite lime, and vermiculite, which is an indication that the mixture contains a high level of organic carbon.

Table 2. Soil(s) Collection, Storage and Properties

Property	Sandy loam soil	Redi-Earth & Seedling Potting Mix
Geographic location	Not reported	
Pesticide use history at the collection site	Not reported	
Collection date	Not reported	
Collection procedures	Not reported	
Sampling depth	Not reported	
Storage conditions	Not reported	
Storage duration	Not reported	
Soil preparation	50% sandy loam soil and 50% Redi-Earth & Seedling Potting Mix (ca. 1 kg)	
Soil texture (USDA):	Not reported	
% Sand	71	Not reported
% Silt	27	Not reported
% Clay	2	Not reported
pH (water)	Not reported	Not reported
pH	Not reported	Not reported
Organic carbon (%)[1]	Not reported	Not reported
Organic matter (%) (LOI)	Not reported	Not reported
CEC (meq/100 g) (Method not reported)	Not reported	Not reported
Soil Moisture Content (%):	*ca.* 20% (target)	
At 0.1 bar (pF 2.0)	Not reported	
At 1/3 bar (pF 2.5)	Not reported	
Bulk density (g/cm^3)	Not reported	
Microbial biomass:		
At initiation	Not reported	
At termination	Not reported	
Soil taxonomic classification (WRB)	Not reported	

Data obtained from p. 16 and Appendix 5, p. 68 of the study report. Sandy loam soil characterized by Agvise Laboratories, Benson, Minnesota.

B. Study Design

1. Experimental Conditions

Closed dome systems (humidomes; Hummert International Humid-Dome clear plastic, Item # 143851000) were configured to capture vapor phase dicamba on plastic cassettes (SKC Inc. Item # 225-2050LF) filled with "Mixed Cellulose Ester" (MCE) filters following the application of the tank mixtures to the soil (pp. 16-17). The humidomes were disposable, plastic, sealed containers that allow for controlled environmental conditions and were modified to allow dicamba sample collection on the MCE filters. Assembled, closed humidomes (10” wide x 20” long) were placed in a temperature and humidity controlled environmental chamber.

On each humidome lid, two holes (*ca.* 1 cm) were punched in the middle of each of the smaller sides of the plastic lid at *ca.* 2-3 inch above the lower rim of the lid. One of the holes was left open, to allow for air intake, while the other hole was plugged with a panel mount & nut obtained from Eldon James (1/4-18 NPSM to 1/4″ Barbed Panel Mount, item # PM4S-4PP; 1/4-18 NPSF Bulkhead/Panel Mount Nut, item # G102-150-18). Air exiting the panel mount entered the SKC filter cartridge with MCE filter. The two openings of the cartridge could be closed with plastic pins. The air left the cartridge, via chemical-resistant Tygon® tubing towards “hovering-ball” airflow meter/adjusters. The airflow was created via a vacuum pump which was attached to the manifold that held six individual airflow adjusters.

Airflow was monitored via a Mesalabs DryCal Defender 520 airflow meter at the beginning and the end of the volatilization period (pp. 16-17). Chamber lights (LED) were programmed to be on for 14 hours and off for 10 hours. Light intensity was not reported. Automated temperature and relative humidity recorders were employed, but the model information was not specified. After *ca.* 24 hours, the PUF samples were removed from the lid of the humidome and the humidome was removed from the environmental chamber.

Table 3. Experimental Design

Parameter		Test 1 Engenia® only (pH tests)	Tests 2-6 Engenia® Tank Mixes	Tests 7-18 Engenia® only (RH and temperature tests)
Duration of the test (hours)		*ca.* 24 for each test		
Soil condition (Air dried/fresh)		*ca.* 20% (target moisture)		
Soil sample weight (g/replicate)		*ca* 1 kg		
Soil depth (cm)		Not reported		
Test concentration (mg ai/kg soil (dry weight))		7.23 mg dicamba/kg (target)		
		7.52 ± 0.73 mg dicamba/kg	7.20 ± 0.47 mg dicamba/kg	7.10 ± 0.52 mg dicamba/kg
Field Equivalent Application Rate (lb a.i./A)		*ca.* 0.5 lb a.e. dicamba/A [15 gallons per acre (GPA) equivalent to 0.5 lb a.e. dicamba/A and 7.23 mg dicamba a.e. per 10” × 20” humidome tray]		
Number of replicates		4 for each of the tank mixes in each pH/temperature/relative humidity test		
		44 replicates total	76 replicates total	40 replicates total
Test apparatus		Closed dome systems (humidomes) configured to capture dicamba on MCE filters.		
Test material application	Test solution volume used/ treatment	1.81 mL (spray solution) per tray (target)		
	Application method	Sprayer equipped with commercial spray jet DB TeeJet Model 95015EVS (color code green) and a conveyer belt at 40 PSI (height above benchtop/soil was not reported). After application, humidome lid was secured onto tray and two air holes were closed to avoid losses.		
Indication of test material adsorbing to walls of test apparatus?		No		

Parameter		Test 1 Engenia® only (pH tests)	Tests 2-6 Engenia® Tank Mixes	Tests 7-18 Engenia® only (RH and temperature tests)
Experimental conditions	Temperature (°C)	30.7 ± 0.7°C	30.2 ± 1.0°C	Tests 7-12: 13.4-42.5°C Tests 13-15: 29.9-31.9°C Tests 16-18: 36.9-42.5°C
	Relative humidity	48.2 ± 3.4%	43.5 ± 2.3%	Tests 7-12: 35.6-48.8% Tests 13-15: 23.9-58.2% Tests 16-18: 24.3-42.3%
	Soil moisture content	20% (target)		
		19.2 ± 1.6%	18.1 ± 0.8%	18.6 ± 1.4%
	Moisture maintenance method	Not reported		
	Air flow through system	2.00 ± 0.10 L/minute (target; individual values not reported)[1]		
	Continuous darkness (Yes/No):	No; 14-hour day light cycle.		
Other observations (if applicable)				

Data obtained from pp. 6, 16-18, 27-31, Tables 3-5, pp. 20-21, Table 13, p. 36, and Tables 17-25, pp. 55-65, of the study report.
1 Note: units reported as "L/minute" on pp. 6, 17, and "L/hour" on pp. 27-31 of the study report.

2. Sampling during Study Period

After 24 hours, the vacuum pump was turned off, and the MCE filter cartridges were removed, plugged with plastic pins, and immediately placed into a freezer (temperature not reported; p. 19).

No soil samples were collected.

Table 4. Sampling Design

Parameter	Description
Air Sampling	
Sample intervals (hrs)	*ca.* 24
Sampling method	MCE filters in plastic cassettes
Desired air flow of sampler (L/min)	2.00 ± 0.10 L/minute (target; individual values not reported)[1]
Sample storage before analysis (Yes/No)?	Not reported; stored frozen (temperature not reported) until shipment for analysis (storage time not reported). Shipped frozen (on dry ice or similar) to analytical lab (Symbiotic Research). After receipt at analytical lab, samples were stored frozen (temperature not reported) and analyzed as soon as possible.

Data obtained from pp. 16-17, 19, 25, of the study report.
1 Note: units reported as "L/minute" on pp. 6, 17, and "L/hour" on pp. 27-31 of the study report.

3. Sample Handling and Storage Stability

After collection, samples were removed from the humidomes, immediately placed into a freezer (temperature not reported; p. 19). Samples were shipped frozen (on dry ice or similar) from Genesis Midwest Laboratories, Wisconsin, to the analytical lab (Symbiotic Research, New Jersey). After receipt at analytical lab, samples were stored frozen (temperature not reported) and analyzed as soon as possible (p. 25).

4. Analytical Procedures

Extraction methods: MCE filter cartridges were uncapped then filled with methanol via BASF's "Disc Analysis Method - Humidome" (pp. 23-24). Via gravity filtration, the MCE filter was dissolved in methanol. An aliquot of the methanol was centrifuged (*ca*. 12,500 rpm for *ca*. 10 minutes). An aliquot of the supernatant was diluted with water prior to LC/MS/MS analysis. If LC pressure build-up continued, a syringe filtration of the methanol extract was employed: an aliquot of the methanol extract was diluted with water then filtered via a syringe fitted with a 0.2 µm PVDF filter after equilibration. Dicamba was quantitated using LC-MS/MS with electrospray ionization in negative ion mode.

Identification and Quantification of Parent Compound: Aliquots of the methanol extracts were analyzed for dicamba using LC-MS/MS under the following conditions (pp. 24-25):

HPLC	Hewlett Packard 1100 Series
Mass Spectrometer	Sciex API 4000
Switching Valve	Not reported
Data Software	Absciex Analyst 1.4.2
Column	Zorbax Eclipse Plus Phenyl-Hexyl (2.1 × 150 mm, 3.5 µm)
Mobile Phase	A: Water:formic acid (1000:1, v:v) B: Methanol: formic acid (1000:1, v:v)

Normal LC Pressure

Time (minutes)	% A	% B	Flow Rate (mL/min.)	Divert
0.0	80	20	0.600	
0.2	80	20	0.600	
4.0	5	95	0.600	
5.0	5	95	0.600	
5.1	80	20	0.600	
10.0	80	20	0.600	Stop

High LC Pressure

Time (minutes)	% A	% B	Flow Rate (mL/min.)	Divert
0.0	60	40	0.400	
0.2	60	40	0.400	
4.0	5	95	0.400	
9.0	5	95	0.400	
9.1	60	40	0.400	
13.0	60	40	0.400	Stop

Column Temperature	50ºC
Autosampler Temp	Not reported
Injection Volume	Not reported
Ionization Mode	ESI, negative ion mode
Curtain Gas	Not reported
Collision Gas	Not reported
Ion Spray Voltage	Not reported
Source Temperature	Not reported
Ion Source Gas 1	Not reported
Ion Source Gas 2	Not reported
Interface Heater	Not reported
Probe Position	Not reported
MRM Transitions	221.0/176.7 Da (Dicamba)
Confirmatory Ions	219.0/174.6 Da (Dicamba)
Declustering Potential	Not reported
Entrance Potential	Not reported
Collision Energy	Not reported
Collision Cell Exit Potential	Not reported

Detection Limits (LOD, LOQ) for the Parent Compound: The limit of quantitation (LOQ) of 6.7 ng/MCE filter (p. 25). The LOQ was based on the signals observed with the calibrations standard (0.2 ng(dicamba)/mL), with the LOQ set to 1/3 of this standard. The limit of detection (LOD) was not reported.

Detection Limits (LOD, LOQ) for the Transformation Products: No transformation products were evaluated in the study.

Instrument performance: A calibration curve based on calibration standards at concentration levels of 0.2-10 ng/mL for dicamba was calculated (pp. 22, 26). Control MCE methanol extracts were used to prepared calibration standards, instead of pure methanol.

Lab recovery, air sampling sorbent material: Average overall recoveries were reported as *ca*. 75% (n=12) and *ca*. 80% (n=12) for MCE filters and *ca*. 98% (n=6) and *ca*. 87% (n=6) for methanol extracts at 0.5 and 5.0 ng dicamba/mL, respectively (individual values not reported; p. 26 and 33). No samples were prepared at the LOQ of the method.

Lab recovery, soils: Not applicable

Breakthrough, air samples: Test substance breakthrough was not investigated.

II. Results and Discussion

A. Study Conditions

Temperature and relative humidity were maintained throughout the study in the environmental chamber (pp. 27-31; Tables 3-5, pp. 20-21; Tables 17-25, pp. 55-65). Soil moisture measured 19.2 ± 1.6%, 18.1 ± 0.8%, and 18.6 ± 1.4% in Test 1, Tests 2-6, and Tests 7-18, respectively, prior to applying test material. During the study, loss of moisture from the soil measured 21.7 ± 5.5% and 26.6 ± 8.4% in Test 1 and Tests 2-6, respectively. Loss of moisture from the soil was not measured in Tests 7-18. Microbial biomass was not evaluated.

B. Data

1. Engenia versus pH

The mass of dicamba, the 24-hour average air concentration, the 24-hour average flux rate, and the percent of applied dicamba collected on the sorbent material for Engenia® at various pHs and at *ca.* 2 SPLM after *ca.* 24 hours are shown in **Table 5**. Air concentrations were calculated assuming a constant air flowrate of 2 L/min over the 24-hour period. Flux rates were estimated assuming the tray area was 20 inches by 10 inches. **Figure 1** depicts the mass of dicamba versus pH, showing a somewhat linear trend with the log of the dicamba mass versus pH. The average temperature was 30.7 ± 0.7 °C and the relative humidity was 48.2 ± 3.4% for the different trials. The study author determined that there was a clear trend of increased volatilization with lowered pH in Engenia® spray solutions and the pH range of 6.0-7.0 corresponded to reduced volatilization. The study author noted that variability (standard deviations) of the replicate data increased with lowered pH/increased dicamba volatility.

Table 5. Volatility of dicamba from soil after *ca.* 24 hours

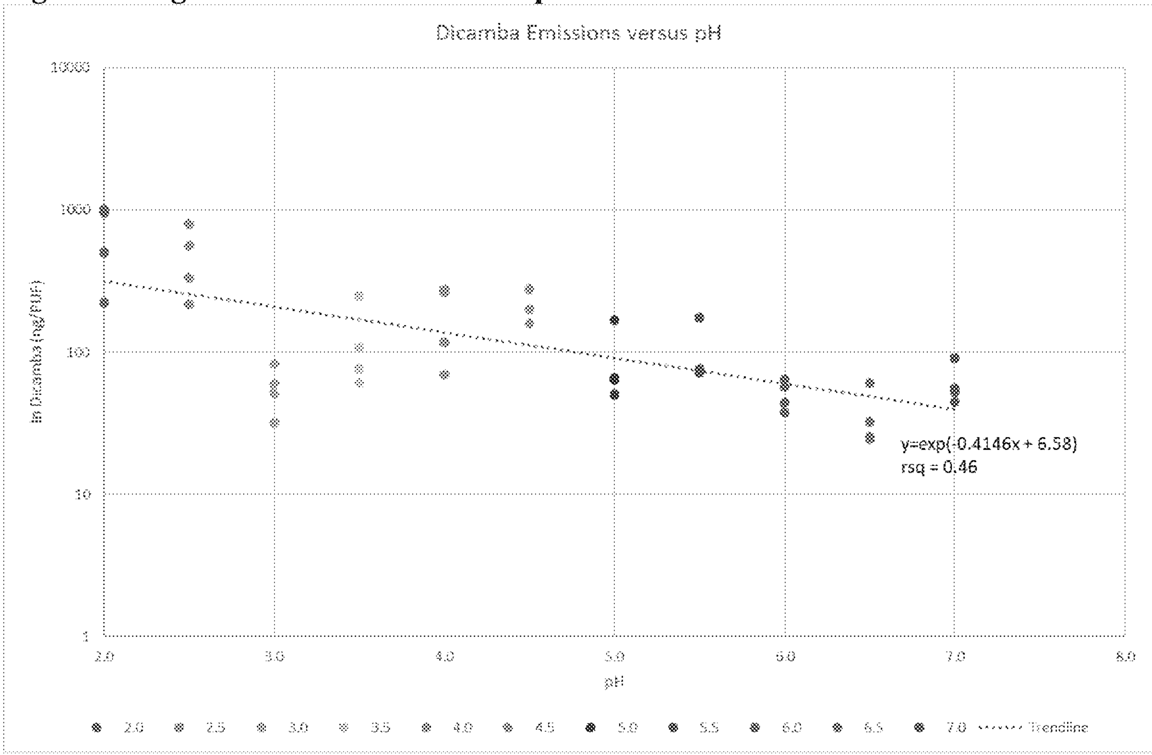
Compound	pH	Measured mass (ng)	24-hour average air concentration[1] (ng/m^3)	24-hour average flux rate[2] (ng/m^2-s)	% of applied dicamba
Parent (dicamba)	2.0	224	77.8	2.01E-02	0.0029
	2.0	506	175.7	4.54E-02	0.0066
	2.0	956	331.9	8.58E-02	0.0125
	2.0	1010	350.7	9.06E-02	0.0132
	2.5	562	195.1	5.04E-02	0.0093
	2.5	796	276.4	7.14E-02	0.0104
	2.5	332	115.3	2.98E-02	0.0043
	2.5	217	75.3	1.95E-02	0.0034
	3.0	59.8	20.8	5.37E-03	0.0008
	3.0	32.0	11.1	2.87E-03	0.0004
	3.0	51.3	17.8	4.60E-03	0.0007
	3.0	83.4	29.0	7.48E-03	0.0012
	3.5	247	85.8	2.22E-02	0.0036
	3.5	60.8	21.1	5.46E-03	0.0008
	3.5	76.5	26.6	6.86E-03	0.0009
	3.5	108	37.5	9.69E-03	0.0013
	4.0	277	96.2	2.49E-02	0.0036
	4.0	69.6	24.2	6.24E-03	0.0010
	4.0	118	41.0	1.06E-02	0.0015

	4.0	267	92.7	2.40E-02	0.0035
	4.5	276	95.8	2.48E-02	0.0038
	4.5	200	69.4	1.79E-02	0.0029
	4.5	282	97.9	2.53E-02	0.0039
	4.5	159	55.2	1.43E-02	0.0021
	5.0	169	58.7	1.52E-02	0.0021
	5.0	66.1	23.0	5.93E-03	0.0009
	5.0	64.5	22.4	5.79E-03	0.0007
	5.0	50.6	17.6	4.54E-03	0.0007
	5.5	176	61.1	1.58E-02	0.0020
	5.5	71.1	24.7	6.38E-03	0.0007
	5.5	76.4	26.5	6.85E-03	0.0010
	5.5	73.8	25.6	6.62E-03	0.0010
	6.0	44.1	15.3	3.96E-03	0.0006
	6.0	57.1	19.8	5.12E-03	0.0008
	6.0	37.6	13.1	3.37E-03	0.0005
	6.0	64.3	22.3	5.77E-03	0.0009
	6.5	25.4	8.8	2.28E-03	0.0003
	6.5	24.4	8.5	2.19E-03	0.0004
	6.5	61.3	21.3	5.50E-03	0.0007
	6.5	32.3	11.2	2.90E-03	0.0004
	7.0	44.9	15.6	4.03E-03	0.0007
	7.0	55.3	19.2	4.96E-03	0.0008
	7.0	52.3	18.2	4.69E-03	0.0007
	7.0	90.7	31.5	8.14E-03	0.0012

Data obtained for measured mass from Table 17, pp. 55-56, flowrate from pp. 6, 27-31, duration from p. 6, and humidome environmental conditions from pp. 27-31 and Tables 3-5, pp. 20-21, of the study report. Note: flow rate units reported as "L/minute" on p. 6 and "L/hour" on pp. 27-31 of the study report.

1. Air concentrations estimated assuming a constant air flowrate of 2 L/min for 24 hours.
2. Flux rates estimated assuming a tray surface are of 20 inches by 10 inches.

Figure 1. Log of Dicamba Mass versus pH



2. Engenia Tank Mixes

The mass of dicamba, the 24-hour average air concentration, the 24-hour average flux rate, and the percent of applied dicamba collected on the sorbent material for Engenia® and various tank mix partners at various pHs and at *ca*. 2 SPLM after *ca*. 24 hours are shown in **Tables 6** through **10**. Air concentrations were calculated assuming a constant air flowrate of 2 L/min over the 24-hour period. Flux rates were estimated assuming the tray area was 20 inches by 10 inches. The average temperature was 30.2 ± 1.0 °C and the relative humidity was 43.5 ± 2.3% for the different trials. **Figures 2** through **6** show a clear trend of decreasing volatilization of dicamba from the tank mixes with pH for all but the Engenia® + Reflex® tank mix, as the pH range for this tank mix was too limited to draw any conclusions. Additionally, the study author reported that adjusting the pH of the spray solution of Engenia® mixed with Reflex below a pH 6.0 was not possible since it caused precipitation (p. 28). Study authors indicated that insufficient data were present to evaluate trends of dicamba volatility based on mixing partner.

Table 6. Volatility of dicamba from soil after *ca*. 24 hours, Engenia® + Cornerstone Plus®

Compound	pH	Measured mass (ng)	24-hour average air concentration[1] (ng/m^3)	24-hour average flux rate[2] (ng/m^2-s)	% of applied dicamba
Parent (dicamba)	2.0	534	185.4	4.79E-02	0.0070
	2.0	578	200.7	5.19E-02	0.0080
	2.0	973	337.8	8.73E-02	0.0151
	2.0	1157	401.7	1.04E-01	0.0160
	4.9	96.7	33.6	8.68E-03	0.0013
	4.9	147	51.0	1.32E-02	0.0019
	4.9	195	67.7	1.75E-02	0.0026
	4.9	334	116.0	3.00E-02	0.0044

	5.5	249	86.5	2.23E-02	0.0036
	5.5	254	88.2	2.28E-02	0.0033
	5.5	2231	--*	--*	--*
	5.5	622	216.0	5.58E-02	0.0077
	7.5	56.1	19.5	5.03E-03	0.0008
	7.5	63.5	22.0	5.70E-03	0.0009
	7.5	77.5	26.9	6.95E-03	0.0010
	7.5	57.5	20.0	5.16E-03	0.0008

Data obtained for measured mass from Tables 18-22, pp. 57-61, flowrate from pp. 6, 27-31, duration from p. 6, and humidome environmental conditions from pp. 27-31 and Tables 3-5, pp. 20-21, of the study report. Note: flow rate units reported as "L/minute" on p. 6 and "L/hour" on pp. 27-31 of the study report.

* Outlier excluded from calculations in the study report. The value could not be calculated by the reviewer since the specific amount of applied dicamba was not reported.

1. Air concentrations estimated assuming a constant air flowrate of 2 L/min for 24 hours.
2. Flux rates estimated assuming a tray surface are of 20 inches by 10 inches.

Table 7. Volatility of dicamba from soil after *ca.* 24 hours, Engenia® + Roundup PowerMax®

Compound	pH	Measured mass (ng)	24-hour average air concentration[1] (ng/m^3)	24-hour average flux rate[2] (ng/m^2-s)	% of applied dicamba
Parent (dicamba)	2.0	234	81.3	2.10E-02	0.0033
	2.0	555	192.7	4.98E-02	0.0077
	2.0	900	312.5	8.07E-02	0.0141
	2.0	794	275.7	7.12E-02	0.0117
	4.7	102	35.4	9.15E-03	0.0015
	4.7	306	106.3	2.75E-02	0.0045
	4.7	203	70.5	1.82E-02	0.0028
	4.7	246	85.4	2.21E-02	0.0034
	5.5	58.8	20.4	5.28E-03	0.0009
	5.5	47.9	16.6	4.30E-03	0.0007
	5.5	58.7	20.4	5.27E-03	0.0009
	5.5	61.2	21.3	5.49E-03	0.0009
	7.5	87.5	30.4	7.85E-03	0.0013
	7.5	1250*	--*	--*	--*
	7.5	61.9	21.5	5.55E-03	0.0009
	7.5	59.7	20.7	5.36E-03	0.0008

Data obtained for measured mass from Tables 18-22, pp. 57-61, flowrate from pp. 6, 27-31, duration from p. 6, and humidome environmental conditions from pp. 27-31 and Tables 3-5, pp. 20-21, of the study report. Note: flow rate units reported as "L/minute" on p. 6 and "L/hour" on pp. 27-31 of the study report.

* Outlier excluded from calculations in the study report. The value could not be calculated by the reviewer since the specific amount of applied dicamba was not reported.

1. Air concentrations estimated assuming a constant air flowrate of 2 L/min for 24 hours.
2. Flux rates estimated assuming a tray surface are of 20 inches by 10 inches.

Table 8. Volatility of dicamba from soil after *ca.* 24 hours, Engenia® + Raptor®

Compound	pH	Measured mass (ng)	24-hour average air concentration[1] (ng/m^3)	24-hour average flux rate[2] (ng/m^2-s)	% of applied dicamba
Parent (dicamba)	2.0	340	118.1	3.05E-02	0.0050
	2.0	230	79.9	2.06E-02	0.0032
	2.0	232	80.6	2.08E-02	0.0032
	2.0	222	77.1	1.99E-02	0.0034
	5.0	232	80.6	2.08E-02	0.0032
	5.0	128	44.4	1.15E-02	0.0016
	5.0	238	82.6	2.14E-02	0.0031

	5.0	235	81.6	2.11E-02	0.0031
	6.5	96.5	33.5	8.66E-03	0.0015
	6.5	127	44.1	1.14E-02	0.0018
	6.5	81.5	28.3	7.31E-03	0.0011
	6.5	102	35.4	9.15E-03	0.0013
	7.5	53.4	18.5	4.79E-03	0.0007
	7.5	53.0	18.4	4.76E-03	0.0007
	7.5	94.9	33.0	8.51E-03	0.0013
	7.5	60.6	21.0	5.44E-03	0.0009

Data obtained for measured mass from Tables 18-22, pp. 57-61, flowrate from pp. 6, 27-31, duration from p. 6, and humidome environmental conditions from pp. 27-31 and Tables 3-5, pp. 20-21, of the study report. Note: flow rate units reported as "L/minute" on p. 6 and "L/hour" on pp. 27-31 of the study report.
1. Air concentrations estimated assuming a constant air flowrate of 2 L/min for 24 hours.
2. Flux rates estimated assuming a tray surface are of 20 inches by 10 inches.

Table 9. Volatility of dicamba from soil after *ca.* 24 hours, Engenia® + Reflex®

Compound	pH	Measured mass (ng)	24-hour average air concentration[1] (ng/m^3)	24-hour average flux rate[2] (ng/m^2-s)	% of applied dicamba
Parent (dicamba)	6.0	37.1	12.9	3.33E-03	0.0005
	6.0	38.7	13.4	3.47E-03	0.0005
	6.0	42.6	14.8	3.82E-03	0.0006
	6.0	40.1	13.9	3.60E-03	0.0006
	6.6	13.9	4.8	1.25E-03	0.0002
	6.6	38.2	13.3	3.43E-03	0.0005
	6.6	15.6	5.4	1.40E-03	0.0002
	6.6	26.4	9.2	2.37E-03	0.0003
	7.5	52.9	18.4	4.75E-03	0.0007
	7.5	55.6	19.3	4.99E-03	0.0009
	7.5	47.8	16.6	4.29E-03	0.0006
	7.5	45.5	15.8	4.08E-03	0.0006

Data obtained for measured mass from Tables 18-22, pp. 57-61, flowrate from pp. 6, 27-31, duration from p. 6, and humidome environmental conditions from pp. 27-31 and Tables 3-5, pp. 20-21, of the study report. Note: flow rate units reported as "L/minute" on p. 6 and "L/hour" on pp. 27-31 of the study report.
1. Air concentrations estimated assuming a constant air flowrate of 2 L/min for 24 hours.
2. Flux rates estimated assuming a tray surface are of 20 inches by 10 inches.

Table 10. Volatility of dicamba from soil after *ca.* 24 hours, Engenia® + Outlook®

Compound	pH	Measured mass (ng)	24-hour average air concentration[1] (ng/m^3)	24-hour average flux rate[2] (ng/m^2-s)	% of applied dicamba
Parent (dicamba)	2.0	906.0	314.6	8.13E-02	0.0125
	2.0	426.0	147.9	3.82E-02	0.0059
	2.0	601.0	208.7	5.39E-02	0.0083
	2.0	632.0	219.4	5.67E-02	0.0087
	5.0	27.6	9.6	2.48E-03	0.0004
	5.0	30.6	10.6	2.75E-03	0.0004
	5.0	28.4	9.9	2.55E-03	0.0004
	5.0	18.3	6.4	1.64E-03	0.0003
	6.5	54.6	19.0	4.90E-03	0.0008
	6.5	53.7	18.6	4.82E-03	0.0007
	6.5	127	44.1	1.14E-02	0.0019
	6.5	47.8	16.6	4.29E-03	0.0007
	7.5	16.9	5.9	1.52E-03	0.0003
	7.5	16.9	5.9	1.52E-03	0.0002

	7.5	26.5	9.2	2.38E-03	0.0004
	7.5	16.2	5.6	1.45E-03	0.0002

Data obtained for measured mass from Tables 18-22, pp. 57-61, flowrate from pp. 6, 27-31, duration from p. 6, and humidome environmental conditions from pp. 27-31 and Tables 3-5, pp. 20-21, of the study report. Note: flow rate units reported as "L/minute" on p. 6 and "L/hour" on pp. 27-31 of the study report.
1. Air concentrations estimated assuming a constant air flowrate of 2 L/min for 24 hours.
2. Flux rates estimated assuming a tray surface are of 20 inches by 10 inches.

Figure 2. Engenia plus Cornerstone Plus Tank Mix versus pH

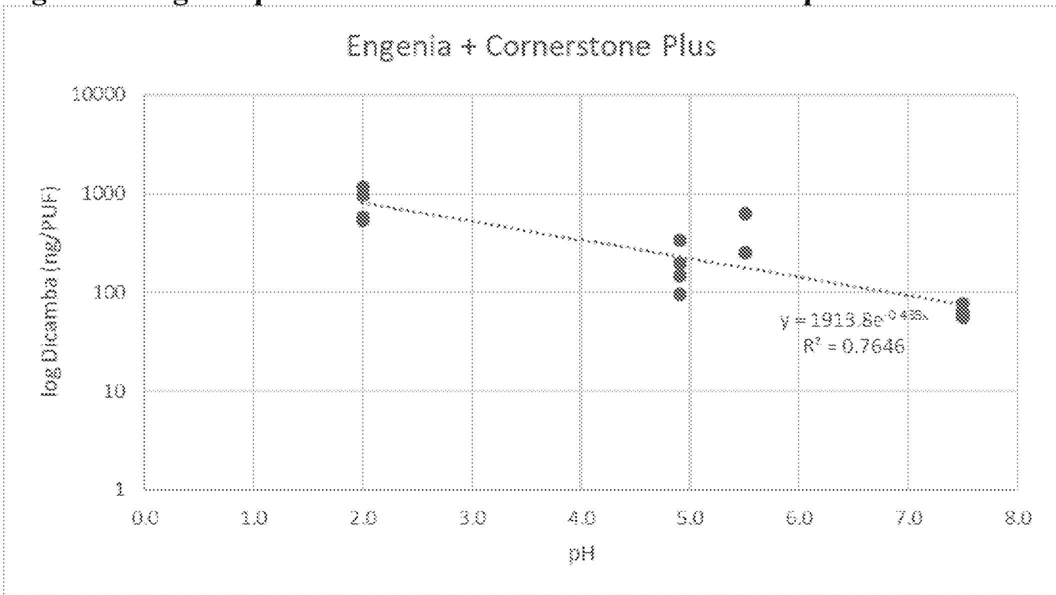


Figure 3. Engenia plus PowerMax Tank Mix versus pH

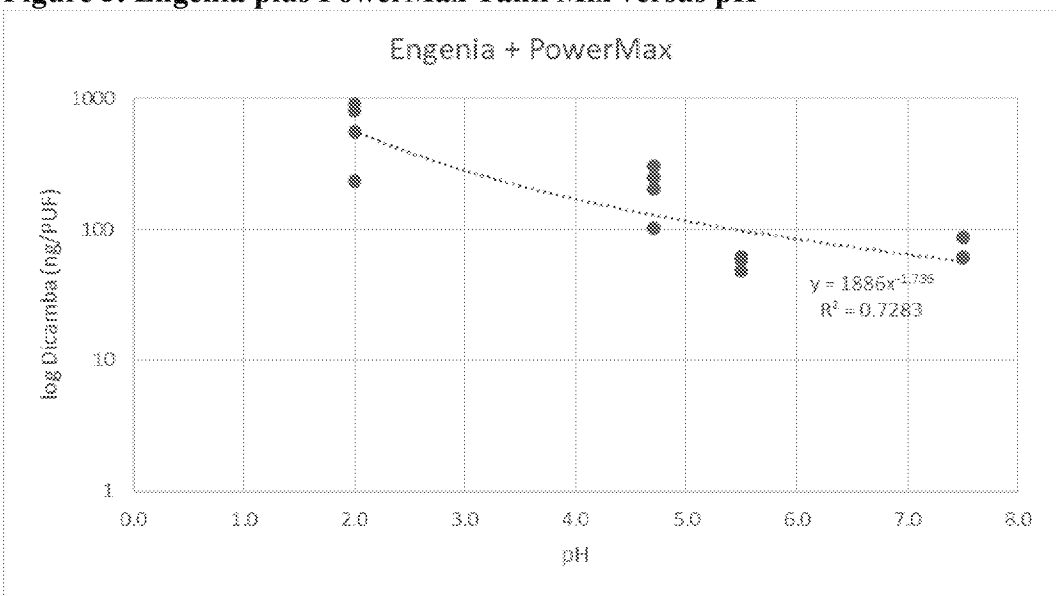


Figure 4. Engenia plus Raptor Tank Mix versus pH

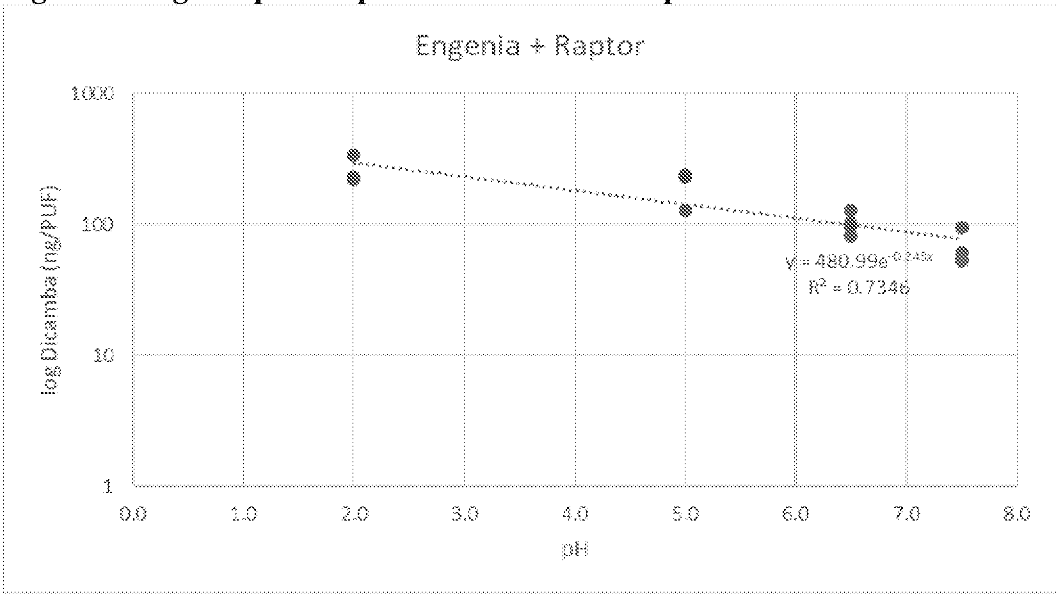


Figure 5. Engenia plus Reflex Tank Mix versus pH

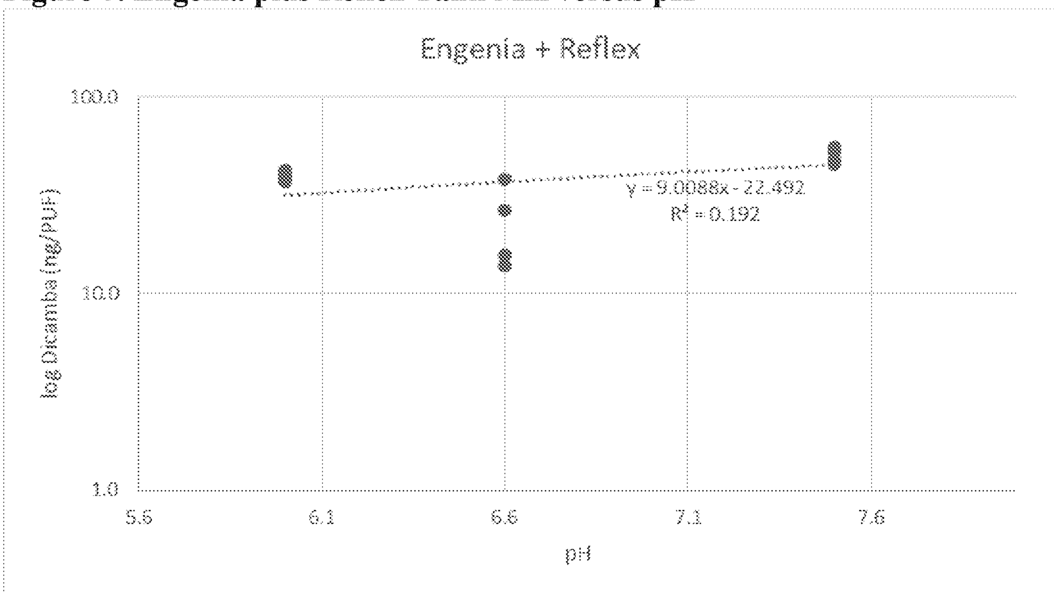


Figure 6. Engenia plus Outlook Tank Mix versus pH

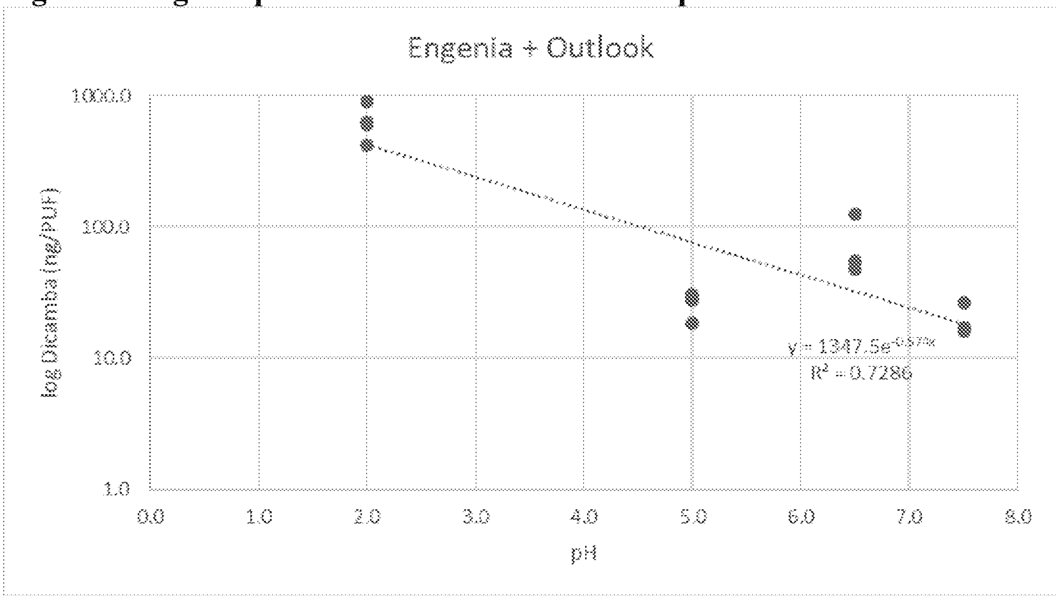
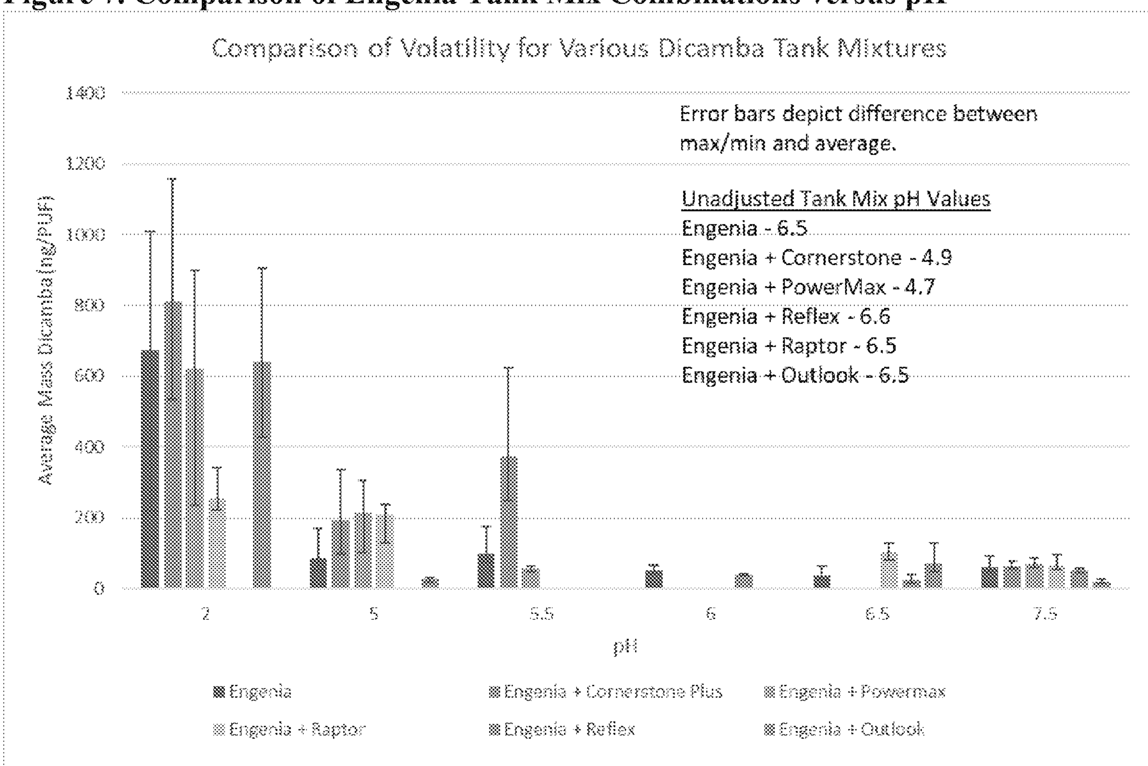


Figure 7 depicts a comparison of the average mass of dicamba volatilized at each pH for the various tank mixes. Based on the unadjusted tank mix pH values, both the addition of Cornerstone Plus and PowerMax resulted in lower pHs (4.7-4.9) than Engenia alone (6.5), while the remaining tank mixes resulted in pH values comparable to that of Engenia alone. And as pH increases, dicamba mass volatilized tends to decrease regardless of the tank mix partner.

Figure 7. Comparison of Engenia Tank Mix Combinations versus pH



3. Engenia versus Temperature and Relative Humidity

The mass of dicamba, the 24-hour average air concentration, the 24-hour average flux rate, and the percent of applied dicamba collected on the sorbent material for Engenia® and various tank mix partners at various pHs and at *ca*. 2 SPLM after *ca*. 24 hours are shown in **Table 11**. **Figures 8** and **9** depict relationships of volatilized dicamba versus relative humidity and temperature. There appears to be a relationship between volatilization and temperature at a constant relative humidity (~40%) and a relationship between volatilization and relative humidity at higher temperatures (~40 °C), but not at lower temperatures (~30 °C). The study author determined that there was a clear trend of increased volatilization with higher temperatures (>40°C) and higher relative humidity with higher temperatures.

Study authors observed that results from the trials indicated that the higher humidity coincided with less water loss during the 24-hour volatilization period, while the higher temperatures showed increased evaporation of water from soil. Based on these observations, study authors concluded that the volatilization of dicamba was not triggered by changes of the vapor pressure (Henry's law) with reduced availability of water, but rather, since dicamba is very water soluble, this potential effect might not be detectable (p. 32).

Table 11. Volatility of dicamba from soil after *ca*. 24 hours, with regards to temperature and relative humidity

Compound	Temperature (°C)	Relative humidity (%)	Measured mass (ng)	24-hour average air concentration[1] (ng/m^3)	24-hour average flux rate[2] (ng/m^2-s)	% of applied dicamba
Parent (dicamba)	13.4	35.6	12.7	4.4	1.14E-03	0.0002%
	13.4	35.6	9.39	3.3	8.42E-04	0.0001%
	13.4	35.6	11.8	4.1	1.06E-03	0.0002%
	13.4	35.6	41.2	14.3	3.70E-03	0.0005%
	20.1	41.3	9.64	3.3	8.65E-04	0.0001%
	20.1	41.3	10.3	3.6	9.24E-04	0.0001%
	20.1	41.3	10.2	3.5	9.15E-04	0.0001%
	20.1	41.3	20.4	7.1	1.83E-03	0.0003%
	23.2	45.5	44.2	15.3	3.97E-03	0.0006%
	23.2	45.5	43.8	15.2	3.93E-03	0.0006%
	23.2	45.5	33.2	11.5	2.98E-03	0.0005%
	23.2	45.5	68.5	23.8	6.15E-03	0.0011%
	29.9	48.8	25.4	8.8	2.28E-03	0.0003%
	29.9	48.8	24.4	8.5	2.19E-03	0.0004%
	29.9	48.8	61.3	21.3	5.50E-03	0.0007%
	29.9	48.8	32.3	11.2	2.90E-03	0.0004%
	35.2	44.3	107.6	37.4	9.65E-03	0.0016%
	35.2	44.3	65.1	22.6	5.84E-03	0.0009%
	35.2	44.3	54.0	18.8	4.84E-03	0.0008%
	35.2	44.3	49.3	17.1	4.42E-03	0.0008%
	42.5	38.1	581	201.7	5.21E-02	0.0084%
	42.5	38.1	477	165.6	4.28E-02	0.0074%
	42.5	38.1	503	174.7	4.51E-02	0.0069%
	42.5	38.1	928	--*	--*	--*
	31.9	23.9	33.6	11.7	3.01E-03	0.0005%
	31.9	23.9	29.5	10.2	2.65E-03	0.0005%
	31.9	23.9	42.7	14.8	3.83E-03	0.0005%

	31.9	23.9	44.0	15.3	3.95E-03	0.0006%
	31.0	58.2	63.5	22.0	5.70E-03	0.0009%
	31.0	58.2	83.8	29.1	7.52E-03	0.0012%
	31.0	58.2	73.2	25.4	6.57E-03	0.0010%
	31.0	58.2	59.4	20.6	5.33E-03	0.0009%
	36.9	24.3	109	37.8	9.78E-03	0.0015%
	36.9	24.3	77.6	26.9	6.96E-03	0.0011%
	36.9	24.3	97.8	34.0	8.77E-03	0.0014%
	36.9	24.3	90.6	31.5	8.13E-03	0.0013%
	40.6	42.3	433	150.3	3.88E-02	0.0059%
	40.6	42.3	654	227.1	5.87E-02	0.0090%
	40.6	42.3	1485	515.6	1.33E-01	0.0216%
	40.6	42.3	796	276.4	7.14E-02	0.0123%

Data obtained for measured mass from Table 23, pp. 62-63, flowrate from pp. 6, 27-31, duration from p. 6, and humidome environmental conditions from pp. 27-31 and Tables 3-5, pp. 20-21, of the study report. Note: flow rate units reported as "L/minute" on p. 6 and "L/hour" on pp. 27-31 of the study report.

* Outlier excluded from calculations in the study report. The value could not be calculated by the reviewer since the specific amount of applied dicamba was not reported.

1. Air concentrations estimated assuming a constant air flowrate of 2 L/min for 24 hours.
2. Flux rates estimated assuming a tray surface are of 20 inches by 10 inches.

Figure 8. Dicamba Volatility as a Function of Relative Humidity

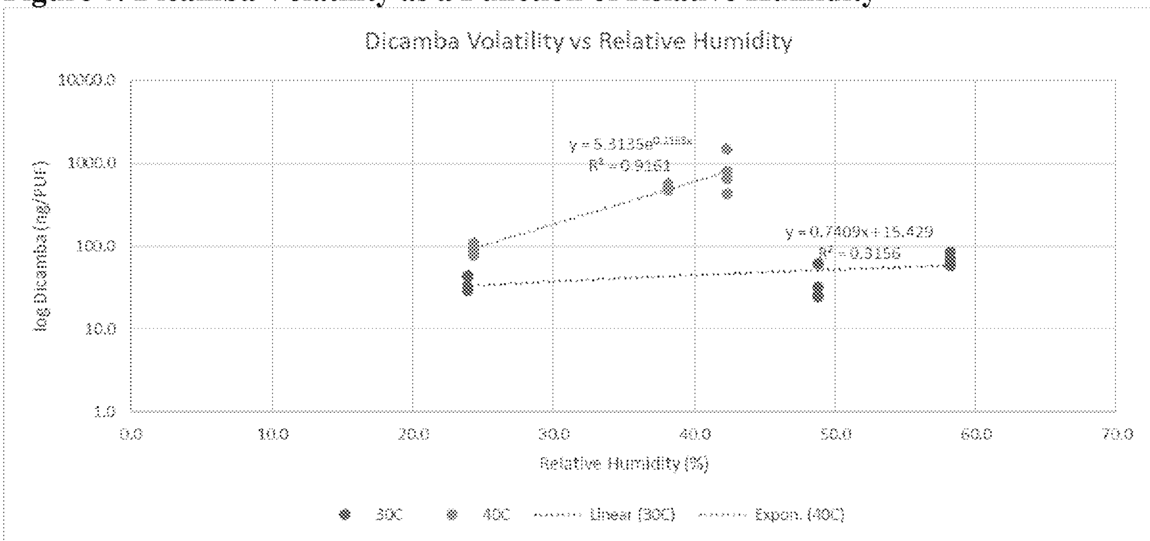
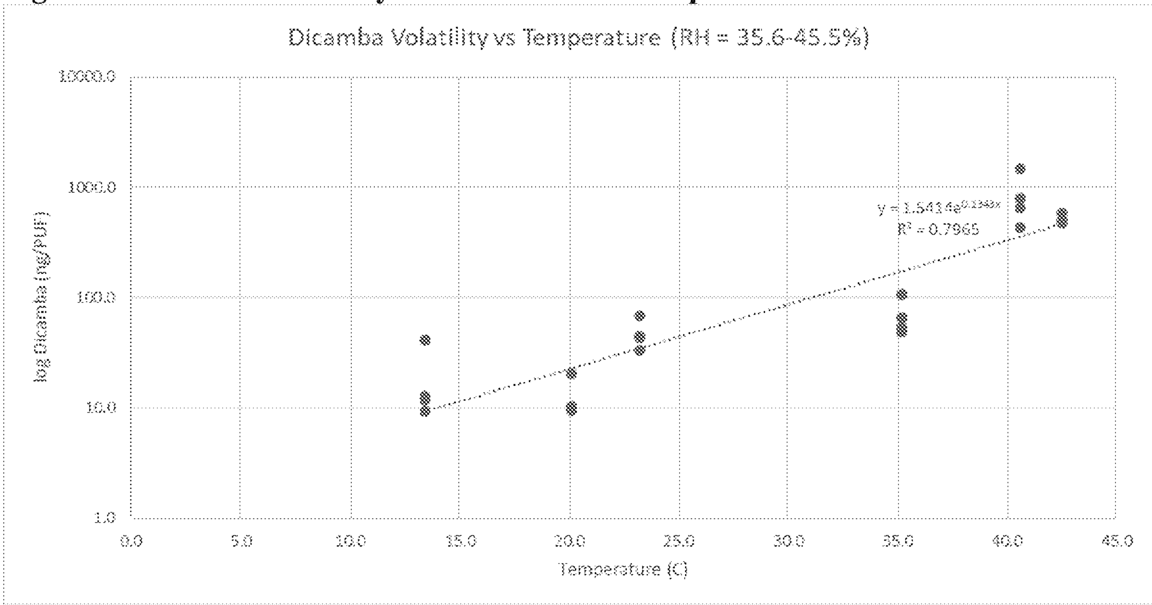


Figure 9. Dicamba Volatility as a Function of Temperature



C. Material Balance

No material balance or distribution of dicamba in the air and soil was calculated in the study.

D. Transformation Products

The study does not address transformation products.

III. Study Deficiencies and Reviewer's Comments

1. The compositions of the test substances were not reported, and test substance storage was not reported.

2. The test soil was only partially characterized. The sandy loam soil was characterized without USDA soil texture classification, and the Redi-Earth & Seedling Potting Mix was not characterized (p. 16; Appendix 5, p. 68). ASTM protocol STP1587, used in the conduct of this study, requires that "In order to minimize variability due to the soil composition, a one to one mixture of US10 field soil and Redi-Earth was used. Although different soil types may impact volatility, using this standard soil mixture helped reduce the impact of this variable." Results of this study should not be used quantitatively except for soils with an organic carbon content greater than or equal to that of peat soil. Differences in volatility should be regarded as relative, not as absolute values.

3. Method validation data was incomplete (p. 26). No samples were prepared at the LOQ of the method. The method LOD was not reported (p. 25).

4. Outliers were excluded by the study report from calculations of % of applied dicamba and plots of mass of dicamba versus test conditions: Test 2 (1 outlier), Test 3 (1 outlier), Test 12 (1 outlier),

and Test 17 (1 outlier; Tables 17-25, pp. 55-65). The mass of dicamba values were typically higher than the others in the replicate.

5. The reviewer could not calculate the % of applied dicamba since applied dicamba per replicate was not reported.

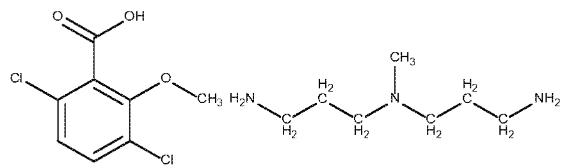
6. The study report stated that it was found that lowering the pH of the spray solution of Engenia® mixed with Reflex below a pH 6.0 was not possible since a precipitate was observed which would have blocked the spray nozzles during spray application (p. 28). The mixtures containing Reflex were only adjusted to a pH of 6.0 and 7.5, plus the unadjusted pH 6.6, for testing.

IV. References

1. Gavlick, W.K., Wright, D.R., MacInnes, A., Hemminghaus, J.W., Webb, J.K., Yermolenka, V.I., and Su, W. 2016. "A Method to Determine the Relative Volatility of Auxin Herbicide Formulations," Pesticide Formulation and Delivery Systems: 35th Volume, ASTM STP1587, G.R. Goss, Ed., ASTM International, West Conshohocken, PA, pp. 24-32.

2. Anonymous (BASF). Disc Analysis Method – Humidome", 2-page document provided by the Sponsor as guidance for the analytical procedures.

DER ATTACHMENT 1. Dicamba BAPMA and Its Environmental Transformation Products. [A]

Code Name/ Synonym	Chemical Name	Chemical Structure	Study Type	MRID	Maximum %AR (day)	Final %AR (study length)
PARENT						
Dicamba BAPMA (N,N-Bis-(3-aminopropyl)methylamine salt of dicamba; Dicamba-biproamine)	**IUPAC:** 3,6-Dichloro-o-anisic acid - N-(3-aminopropyl)-N-methylpropane-1,3-diamine (1:1) **CAS:** 3,6-Dichloro-2-methoxybenzoic acid compound with N^1-(3-aminopropyl)-N^1-methyl-1,3-propanediamine (1:1) **CAS No.:** 1286239-22-2 **Formula:** $C_{15}H_{25}Cl_2N_3O_3$ **MW:** 366.28 g/mol **SMILES:** NCCCN(C)CCCN.ClC1=CC=C(Cl)C(C(O)=O)=C1OC		Non-guideline	51049001	NA	NA
MAJOR (>10%) TRANSFORMATION PRODUCTS						
No major transformation products were identified.						
MINOR (<10%) TRANSFORMATION PRODUCTS						
No minor transformation products were identified.						
REFERENCE COMPOUNDS NOT IDENTIFIED						
All compounds used as reference compounds were identified.						

[A] AR means "applied radioactivity". MW means "molecular weight". NA means "not applicable".

Attachment 2: Statistics Spreadsheets and Graphs

100094_51049001_DE
R-Fate_NG_06-08-20.x